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Oxygen reduction in acid media: effect of iron substitution by cobalt on heat-treated naphthalocyanine impregnations supported on preselected carbon blacks

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Abstract

FeNpc(1.2) impregnations were investigated at various loadings using a rotating-disk electrode, voltammetry and X-ray photoelectron spectroscopy (XPS) techniques. Optimal activity takes place at monolayer coverage, and major demetallation occurs after prolonged exposure to acid solution. The substitution of Fe by Co enables the electrochemical performances to reach those presented by 10% Pt on Vulcan and stops the demetallation process. The application of fast atomic bombardment secondary ion mass spectrometry (FABS) together with XPS sheds light on the detrimental role of some electrophilic groups attached to the carbon black-catalyst interface.

INTRODUCTION

Co and Fe macrocyclic compounds are still a topic of interest as possible substitutes for Pt-based catalysts in air generator applications. Encouraging data at three-phase electrodes have recently been reported [1]. Performances comparable with those of Pt electrodes were found after pyrolysis of polypyrroles on carbon supports containing Fe and Co salts [2]. This activity was correlated with the formation of MeN₄ units. Quantum chemical calculations have shown that, of the

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various macrocyclic compounds, Co and Fe porphyrins appear to be the most suitable candidates for O_2 reduction [3]. However, the effect of the support was not considered in this work. Improvement of the electrocatalytic properties of such materials on carbon supports appears to depend crucially on the effect of heat treatment [4].

In the case of phthalocyanines [5], dispersion seems to play an important rôle in the formation of ionized states with O_2 . The stacking of several layers of Co porphyrins turns out to be beneficial for O_2 reduction in alkaline media [6]. In acid media relatively high activities were obtained on glassy carbon coated with films consisting of three to 80 layers of polymerized Co porphyrins [7]. Therefore the catalyst dispersion may present an optimal value which may be different for Co and Fe macrocycles.

Relatively few spectroscopic techniques can be used to provide an insight into the catalyst layer structure on carbon supports, particularly for the investigation of heat treatment effects. Extended X-ray absorption fine structure (EXAFS) measurements after heat treatment at various temperatures have shown that the optimal activity coincides with the conservation of the square planar structure of the metal [8,9]. However, as factors such as the dispersion of the catalyst and its interface with the carbon blacks seem to be very important in the determination of electrocatalytic performance, the X-ray photoelectron spectroscopy (XPS) technique may prove to be useful. The recent availability of fast atomic bombardment secondary ion mass spectrometry (FABS) equipment also provides new information on the nature of the species present at the catalyst-support interface.

The behavior of FeNPc(1.2), which is a mixture of four isomers, or FeNPc(2.3), which is a single isomer, deposited on various active charcoals such as Norit BRX or carbon blacks has been investigated before and after heat treatment by a number of workers [10–13]. The aim of the present paper is to compare different loadings of FeNPc(1.2) impregnation on the same active selected support (Printex XE2) with equivalent loadings of CoNPc(1.2) in order to examine the rôle of the central ion on the activity for O_2 reduction in an acid medium.

EXPERIMENTAL

Preparation and characterization

The preparation and characterization of various FeNPc(1.2) samples on Printex XE2 supports were achieved by similar procedures to those described in ref. 10. They involve heating various amounts of DCN(1.2) powder mixed with Fe acetyl acetonate ($Fe(AcAc)_2$) in a mole ratio of 4 DCN to 1 Fe with carbon black powder in a sealed tube. The characterization is performed by dissolving the impregnated material in pyridine and comparing the spectra with those of the pure powder. The amounts of iron found by atomic absorption spectroscopy are given in Table 1. The samples of supported and pure CoNPc(1.2) powder were prepared and characterized using the same procedure but with Co acetylacetonate $Co(AcAc)_2$.

TABLE 1

Loading of FeNPc samples

Sample	Fe/%	Loading/% w/w
1	0.88–0.94	12–12.9
2	2.05–2.26	28–31
3	2.85–3.06	39–42

Elemental analysis of naphthalocyanines shows that the reaction producing CoNPc(1.2) is more efficient than that producing FeNPc(1.2). The ratio $\text{CoNPc}(1.2)/[\text{H}_2\text{NPc}(1.2) + \text{CoNPc}(1.2)]$ is greater than 93% whereas it is about 60% in the case of FeNPc.

To our knowledge, no UV–Vis spectra of CoNPc(1.2) compounds (supported or unsupported) have been published prior to this investigation. The spectra obtained after exposure to O_2 and prolonged (4 h) exposure to N_2 are shown in Figs. 1(a) and 1(b) respectively. The same operating conditions (e.g. CoNPc(1.2) concentration in pyridine and cell path length) were used in both cases. The main differences between Figs. 1(a) and 1(b) occur in the Soret band with the emergence of additional peaks after exposure to O_2 . These transitions are characteristic of charge-transfer processes taking place between the metal ion (Co^{2+}) and the ligand in metalloporphyrins [14–16]. Therefore a ligand modification due to the attachment of an O_2 molecule which would act as an electron acceptor from the metal ion center is suggested.

In order to check the compounds synthesized, FABS experiments were conducted. Mass spectra were obtained using a Finningan MAT 90 spectrometer equipped with a PDP 11/73 data system. The FABS measurements were carried out using an Ion Tech atomic gun unit, operating at 8 kV and 1 mA (gun current). The target sizes correspond to standard equipment. Figure 2 (in the positive mode) reveals that the main component of the sample is CoNPc(1.2). The vacromium target was filled with the sample (approx. 2 mg) and 2 μl of n-nitrobenzylalcohol (NBA) as matrix and bombarded with a beam of xenon gas. The ions produced in this process were accelerated with a voltage of 5 kV and analyzed by scanning the mass range from m/z 50 to m/z 1200 in 7 s with a resolution of 800 which is more than enough to characterize the molecules concerned here. Each compound was examined in a positive or negative mode depending upon the sign of the acceleration voltage. Each measurement was the average of six scans.

The amount of cobalt in supported samples was determined by atomic absorption spectroscopy, and yielded a CoNPc(1.2) coverage loading of 25%–28% w/w, comparable with sample 2 of FeNPc(1.2).

Electrochemical equipment

The electrochemical equipment is identical with that described elsewhere [10–12]. The electrolyte consists of a solution of sulfuric acid (0.25 M H_2SO_4). The

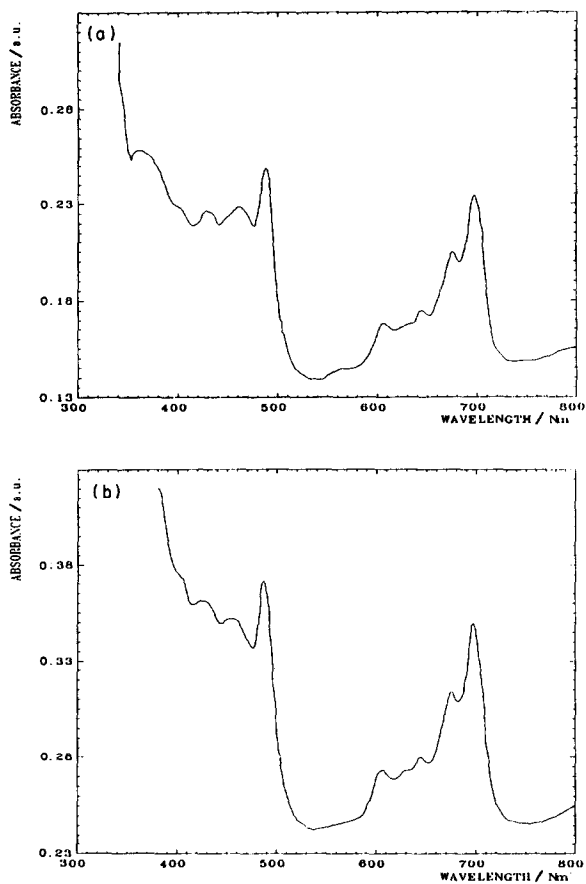


Fig. 1. UV-Vis spectra of CoNPc after exposure to (a) O_2 and (b) N_2 .

surface area of the electrode is 0.125 cm^2 . The potentials are quoted with respect to the reversible hydrogen electrode (RHE).

Electrode preparation

The preparation of the rotating-disk electrode was also identical with that described in refs. 10–12. It consisted in fixing the carbon black impregnations in the disk cavity with a Teflon binding agent. The electrical contact was achieved by gold lacquer.

Sample 1 has been investigated earlier [13]. The present work is concerned with samples 2 and 3 from Table 1 and with CoNPc(1.2) impregnations at about the same loading as sample 2. These impregnations were best for about 10 days in an

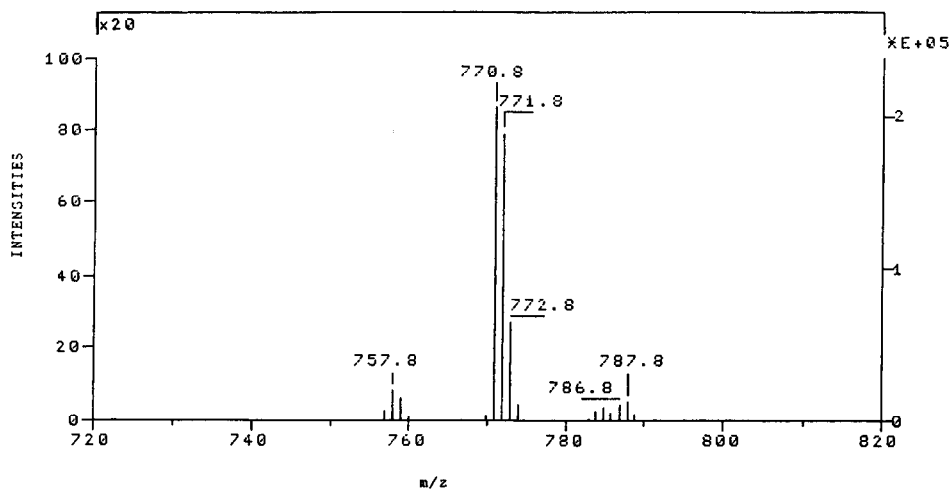


Fig. 2. FAB/MS spectrum of pure CoNPc(1.2) powder (positive mode).

oxygenated sulfuric acid medium (0.25 M) in order to stabilize. The samples were examined before and after heat treatment at 500°C for 2 h under nitrogen.

XPS experiments

In order to obtain an insight into the influence of the substrate on the electrocatalytic behavior of the samples, XPS investigations using an HP 5050 monochromatized spectrometer were performed [10–12] on samples which had been stored for 10 days in 0.25 M H_2SO_4 solution under oxygen.

RESULTS AND DISCUSSION

Effect of the loading on FeNPc(1.2) impregnations

Figures 3(a) and 3(b) show $I-E$ curves for O_2 reduction at various rotation frequencies f on non-heat-treated FeNPc(1.2) impregnations at 30% and 40% loadings respectively. These curves are corrected from the current under nitrogen and identical activities can be seen. The data can be compiled using a Koutecky–Levich plot [17] ($1/I$ vs. $f^{-1/2}$). The total number N of exchanged electrons is found from the slope to be 3.5. In addition, it has been shown [18] that curves of this shape are characteristic of a reaction mechanism involving a limiting adsorption step.

The voltammograms at various scanning velocities under O_2 and N_2 are presented in Figs. 4(a) and 4(b) for FeNPc(1.2) impregnations at 30% loadings. Under O_2 a hump identical with those reported previously [10–13] can be observed. On the basis of the voltammograms, a redox mechanism cannot be

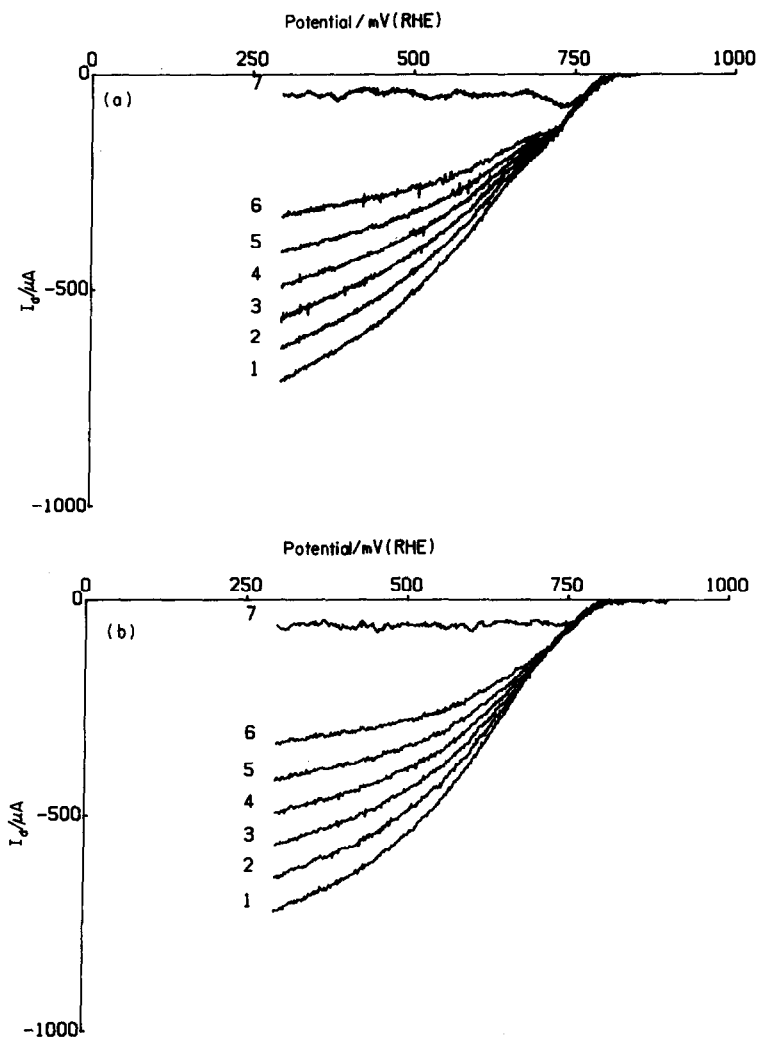


Fig. 3. I - E curves (corrected from the current under N_2) at various rotation frequencies for O_2 reduction on non-heat-treated FeNPc(1.2) loaded at (a) 30% and (b) 40% (scanning velocity, 1.5 mV s^{-1}): (1) 64 rev s^{-1} ; (2) 49 rev s^{-1} ; (3) 36 rev s^{-1} ; (4) 25 rev s^{-1} ; (5) 16 rev s^{-1} ; (6) 9 rev s^{-1} ; (7) 0 rev s^{-1} .

invoked because the position of the cathodic peak is negative with respect to the beginning of O_2 reduction. For 40% loadings the voltammograms under O_2 and N_2 present a similar shape but with a charge density roughly half the size which can be attributed to an effect of the double-layer capacity.

Figure 5 shows, as a reference, I - E curves for the same rotation frequencies as those used above obtained on FeNPc(1.2) loaded at 10% corrected from the curve

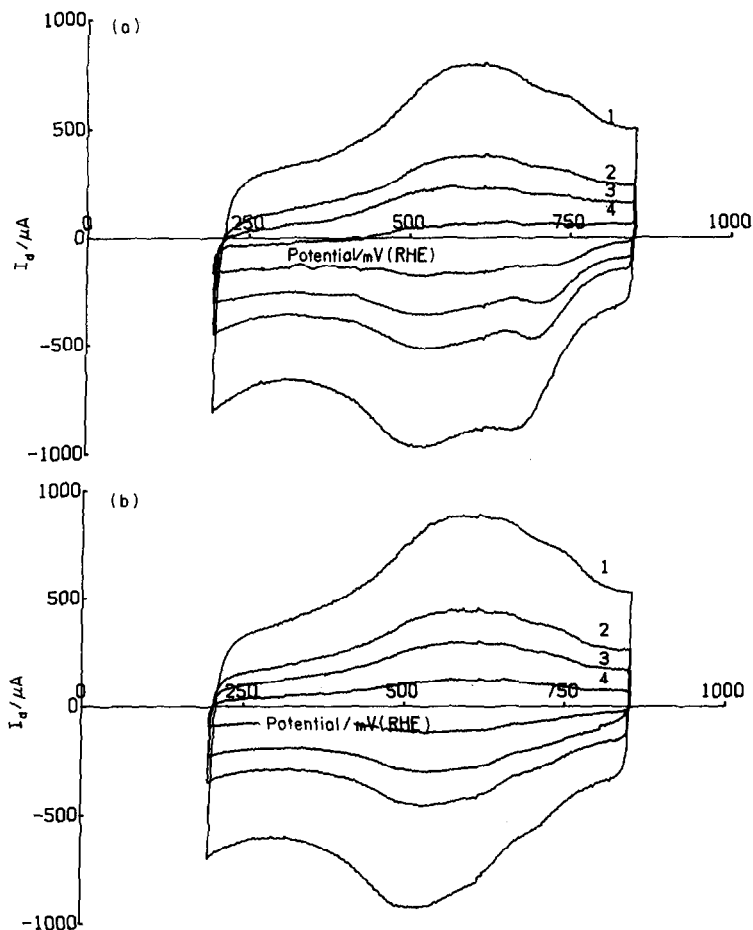


Fig. 4. Voltammograms obtained at a stationary electrode on non-treated FeNPc(1.2) with 30% loading at various scanning velocities under (a) O_2 and (b) N_2 : (1) 10.8 mV s^{-1} ; (2) 5.4 mV s^{-1} ; (3) 3.6 mV s^{-1} ; (4) 1.5 mV s^{-1} . The scans were recorded after electrode stabilization.

under N_2 . These samples were investigated previously [13]. It should be noted that there is a limiting current which obeys the Levich plot I_L vs. $f^{1/2}$ and the relationship

$$E \propto \log[I/(I_L - I)]$$

with a slope of 105 mV per decade characteristic of a diffusion-limiting step coupled with a one-electron transfer.

Therefore the electrochemical activity on non-heat treated samples of FeNPc(1.2) reached a maximum at a loading of about 10%. For higher values the kinetics are modified mainly through a deceleration of the O_2 adsorption step. At a loading of 30% the activity is stabilized.

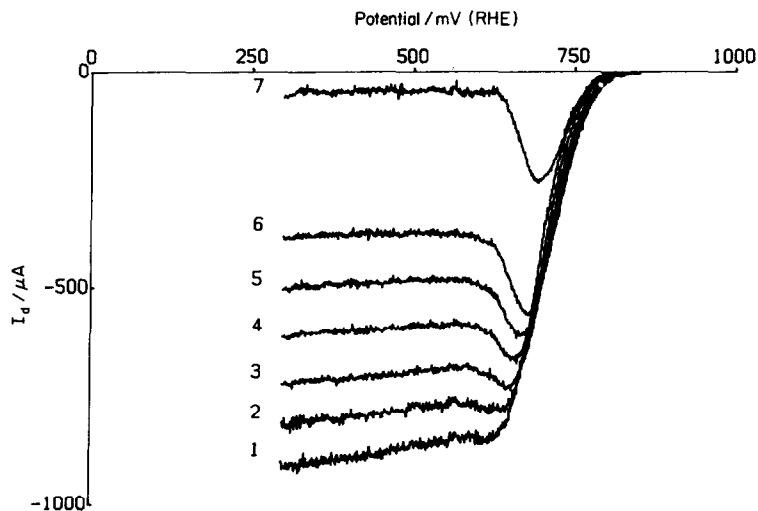


Fig. 5. $I-E$ curves at various rotation frequencies for O_2 reduction on non-heat-treated FeNPc(1.2) with 10% loading. Same conditions as Fig. 3.

The effect of heat treatment on different FeNPc(1.2) loadings is shown in Fig. 6 for the same rotation frequency of 64 rev s^{-1} . The samples loaded at 10% remain the most active, whereas those loaded at 40% are unaffected. In the region of transfer limitation, the current at 30% loading is about half that at 10% loading.

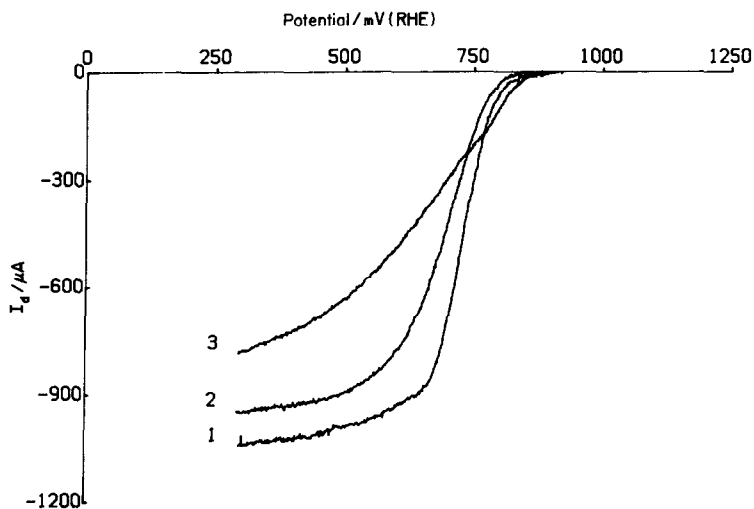


Fig. 6. $I-E$ curves obtained at 64 rev s^{-1} for O_2 reduction on heat-treated FeNPc(1.2) impregnations at different loadings. (1) 10%; (2) 30%; (3) 40%. Scanning velocity 1.5 mV s^{-1} .

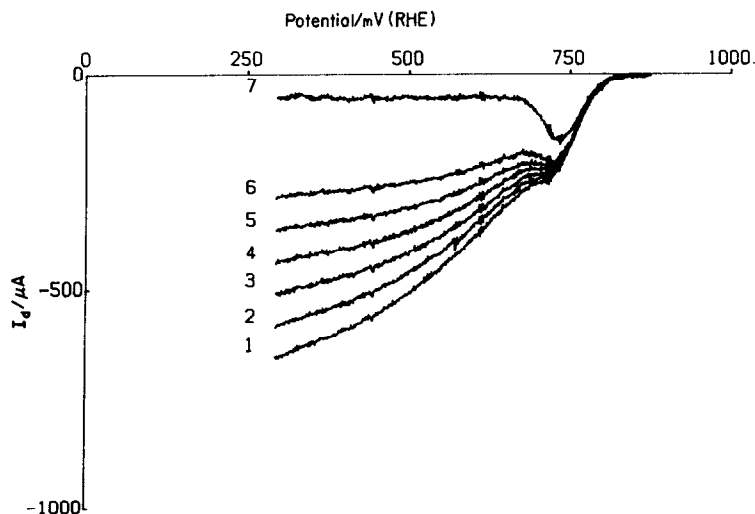


Fig. 7. $I-E$ curves obtained under the same conditions as Fig. 3 for O_2 reduction on non-heat-treated CoNPc(1.2) samples at 27% loading. Rotation frequencies as in Figs. 3(a) and 3(b).

This result can be interpreted in terms of either a partially blocked electrode [19] or a diminution of the transfer kinetic constant.

CoNPc(1.2) samples (27% loading)

Figure 7 shows $I-E$ curves for O_2 reduction on non-heat-treated CoNPc(1.2) samples at 27% loading obtained under the same conditions as Fig. 3. The major difference is the improved activities at potentials more positive than about 650 mV/RHE. Otherwise these curves are similar to those obtained on FeNPc(1.2) at 30% or 40% loadings, and the same conclusions can be drawn concerning the kinetic processes involved.

The voltammograms obtained for non-heat-treated CoNPc(1.2) samples under O_2 and N_2 are shown in Figs. 8(a) and 8(b) respectively. Whereas no peak is visible in Fig. 8(b), the O_2 adduct with higher intensity, which is also present in the UV-Vis spectra (Fig. 1), can be seen in Fig. 8(a) and can explain the improved activities found in this potential domain compared with the Fe samples. The comparison of these voltammograms with $I-E$ curves supports the conclusion drawn above that there is no redox process in the reaction path.

$I-E$ curves for O_2 reduction on heat-treated CoNPc(1.2) samples at 27% loading are shown in Fig. 9(a) for the same conditions as Fig. 3(a). The most salient feature is the existence of a limiting current I_L obeying the Levich relationship $I_L \propto f^{1/2}$. E vs. $\log I/(I_L - I)$ plots are obtained with a slope of 65 mV per decade.

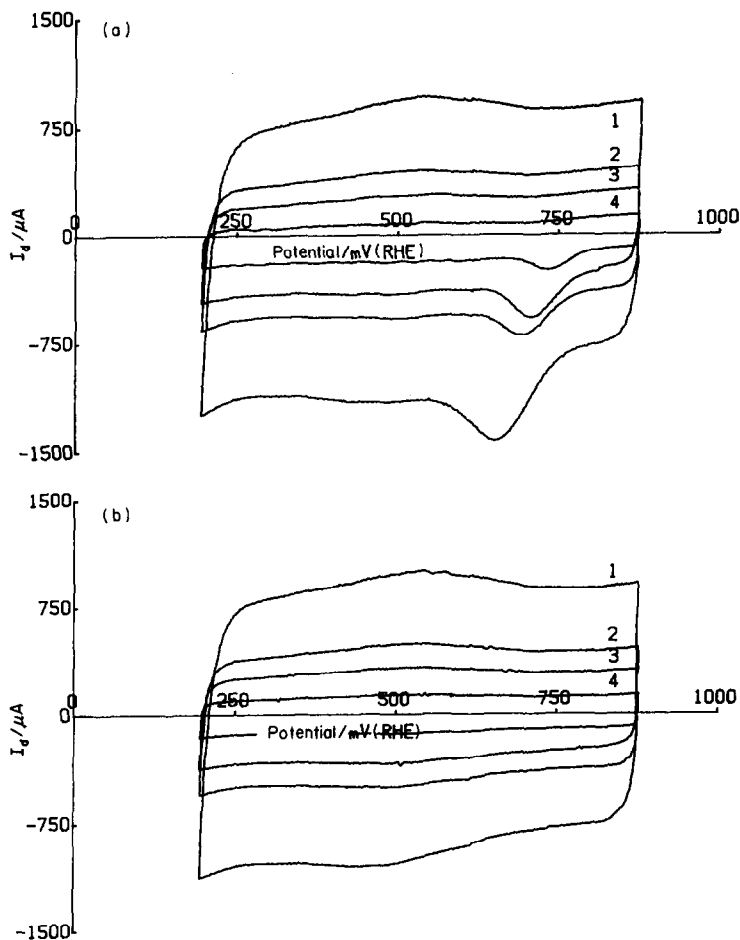


Fig. 8. Voltammograms obtained under the same conditions as Fig. 4 for non-heat-treated CoNPc(1.2) samples at 27% loading under (a) O_2 and (b) N_2 .

It is instructive to compare the data obtained at 64 rev s^{-1} with those obtained under the same conditions for 10% w/w Pt on Vulcan (Fig. 9(b)). They also exhibit a limiting current with a potential $E_{1/2}$ (E at $I_L/2$) identical with that for the CoNPc(1.2) samples loaded at 27%. It should be noted that in the potential domain 700–800 mV/RHE the activities are almost the same for both samples. In the same potential range CoNPc(1.2) samples loaded at 27% display higher charge densities than FeNPc(1.2) samples loaded at 10% and above.

Voltammograms obtained on heat-treated CoNPc samples loaded at 27% are presented in Figs. 10(a) and 10(b) for O_2 and N_2 respectively under the same conditions as in Figs. 4(a) and 4(b). Compared with the voltammogram under O_2 (Fig. 8(a)) the intensity of the peak due to the oxygen adduct in Fig. 10(a) should

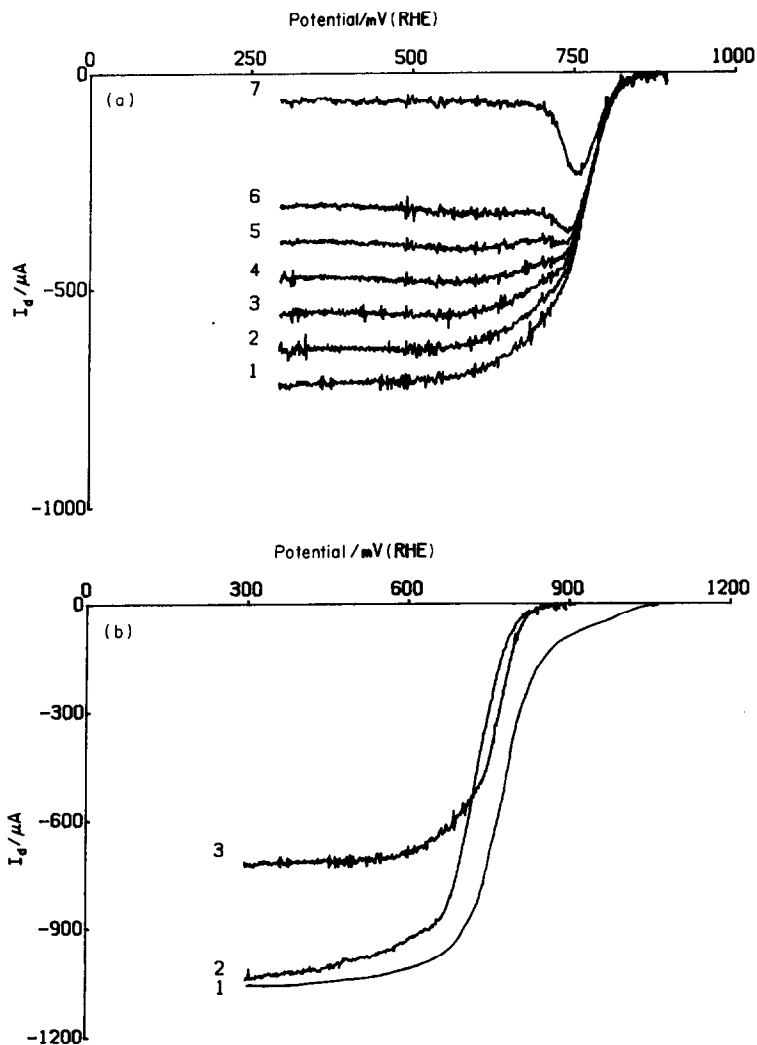


Fig. 9. (a) $I-E$ curves for O_2 reduction of heat-treated CoNPc(1.2) samples at 27% loading under the same conditions as in Fig. 3. (b) Comparison of these samples with 10% w/w Pt on Vulcan under the same conditions (rotation frequency, 64 rev/s): (1) 10% w/w Pt on Vulcan; (2) heat-treated 10% w/w FeNPc on Printex XE2; (3) heat-treated 27% w/w CoNPc(1.2) on Printex XE2.

be noted. It suggests an increased O_2 uptake due to the heat treatment. The voltammograms under N_2 are remarkably flat, thus ruling out any possibility of a redox process in the O_2 reduction pathway.

XPS measurements

The effect of heat treatment on FeNPc(1.2) samples loaded at 10% has been examined using XPS techniques in previous work [13]. The average number n of

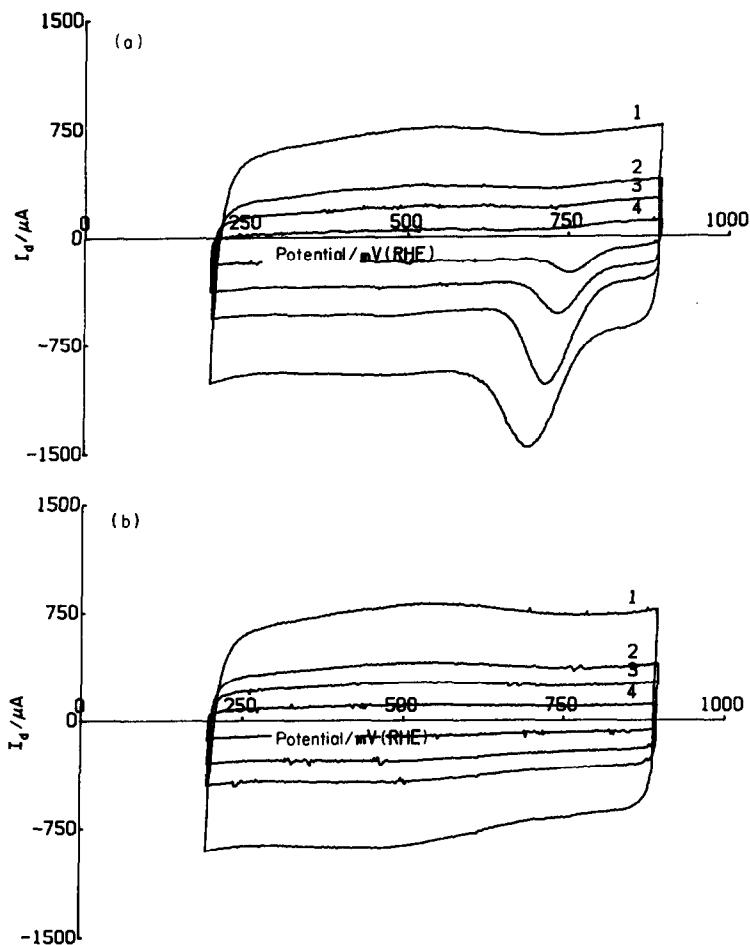


Fig. 10. Voltammograms obtained under the same conditions as Fig. 4 on heat-treated CoNPC(1.2) samples at 27% loading under (a) O₂ and (b) N₂.

catalyst layers on the support can be calculated from [20]

$$\frac{I_e}{I_{e_\infty}} = \frac{rL}{100A_s d} \frac{1 - \exp(-ns/\lambda)}{ns} \quad (1)$$

where $A_s/\text{cm}^2 \text{g}^{-1}$ is the specific surface area of the support, $d \approx 2 \text{ g cm}^{-3}$ is the density of the element, $r \approx 4$ is the roughness factor [20], $\lambda = 20\text{--}25 \text{ \AA}$ is the electron mean free path in the carbon substrate [9], $s = 3.5 \text{ \AA}$ is the thickness of a layer, L is the loading (in wt.% of the element), I_e is the intensity from a very thin layer and I_{e_∞} is the intensity from the bulk material.

Equation (1) holds only if the thickness of the crystallites is less than the electron mean free path in the catalyst layers, e.g. 20 \AA which is equivalent to four

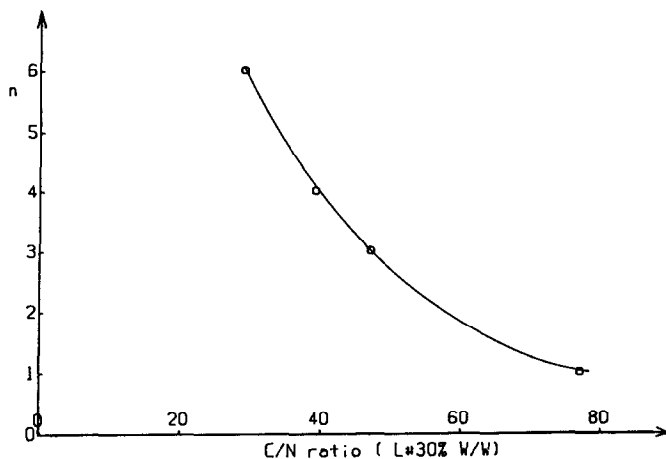


Fig. 11. Representation of n (catalyst layer number) as a function of the C/N ratio (from eqn. (1)).

or five layers. According to eqn. (1), larger crystallites would yield an average n below its real value. At a constant loading value an increase of n resulting from the application of eqn. (1) implies a redistribution of the crystallites on the surface.

The different atomic ratios for the various FeNPc(1.2) impregnations are determined according to the methods of Elliot et al. [22]. From eqn. (1) it is possible to express n as a function of the C/N ratio (Fig. 11).

FeNPc(1.2) samples

The different atomic ratios for FeNPc(1.2) samples at various loadings after storage for 10 days in H_2SO_4 solution are given in Table 2. From this table, it can be seen that the optimum activity is reached for monolayer coverage, which is realized for 10% loading after heat treatment. According to the electrochemical data, for $n > 1$ the O_2 active adsorption step is impeded and the electrode activities are independent of the catalyst thickness. It should be noted that despite

TABLE 2

Atomic ratios for various FeNPc loadings

	Non-treated 10%	Heat-treated		
		10%	30%	40%
C/Fe	2000	2600	1215	773
C/N	62	77	39	29
C/O	46	34	37	29
N/Fe	32	34	31	27
O/N	1.35	2.26	1.05	1
n	2	1	4	6

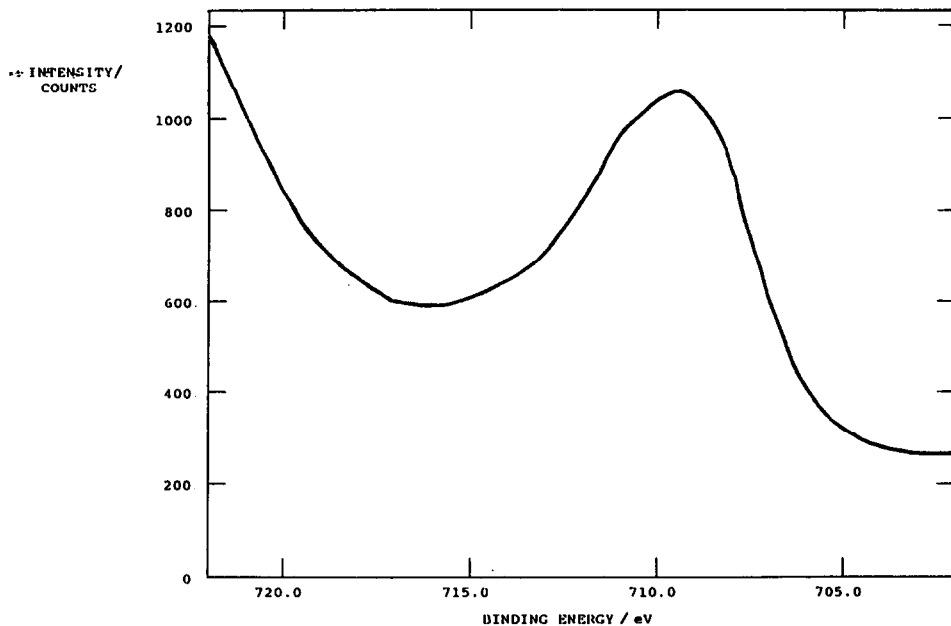


Fig. 12. Fe 2p spectrum (counts versus binding energies) of FeNPc(1.2) samples loaded at 30% or 40%.

the increase in n the N/Fe ratio characteristic of demetallation does not vary significantly. This fact supports the view of proton penetration in the catalyst layers enabling the demetallation process to take place.

The Fe 2p spectra of the samples loaded at 30% and 40% are similar to those shown in Fig. 12. A mixture of Fe(II) and Fe(III) is obtained.

The C/O ratios given in Table 2 clearly show an oxygen uptake due to the heat treatment. As n increases, some oxygen appears to be inserted into the catalyst layers, but this process has little influence on the activity. The O 1s spectra are similar to those of bound oxygen reported in ref. 13. The N 1s spectra are also very similar to those shown for heat-treated samples loaded at 10%. The ratios $I_{400.1}/I_{398.5}$ of the intensity peaks, which are 0.52 and 0.45 respectively for samples loaded at 30% and 40% (Fig. 13), lie close to those reported [4] for the most active samples.

Therefore in the case of FeNPc(1.2) impregnations, the main correlation of the XPS data with the electrochemical activities concerns the value of n . The optimal activity occurs at monolayer coverage, shedding some light on a special configuration composed of the FeN_4 unit fixed at the carbon black surface.

CoNPc(1.2) samples

Table 3 shows the atomic ratios for both untreated and heat-treated CoNPc(1.2) samples before and after storage for 10 days in 0.25 M H_2SO_4 solution. The data were determined using the method of Elliot et al. [22]. The major difference from

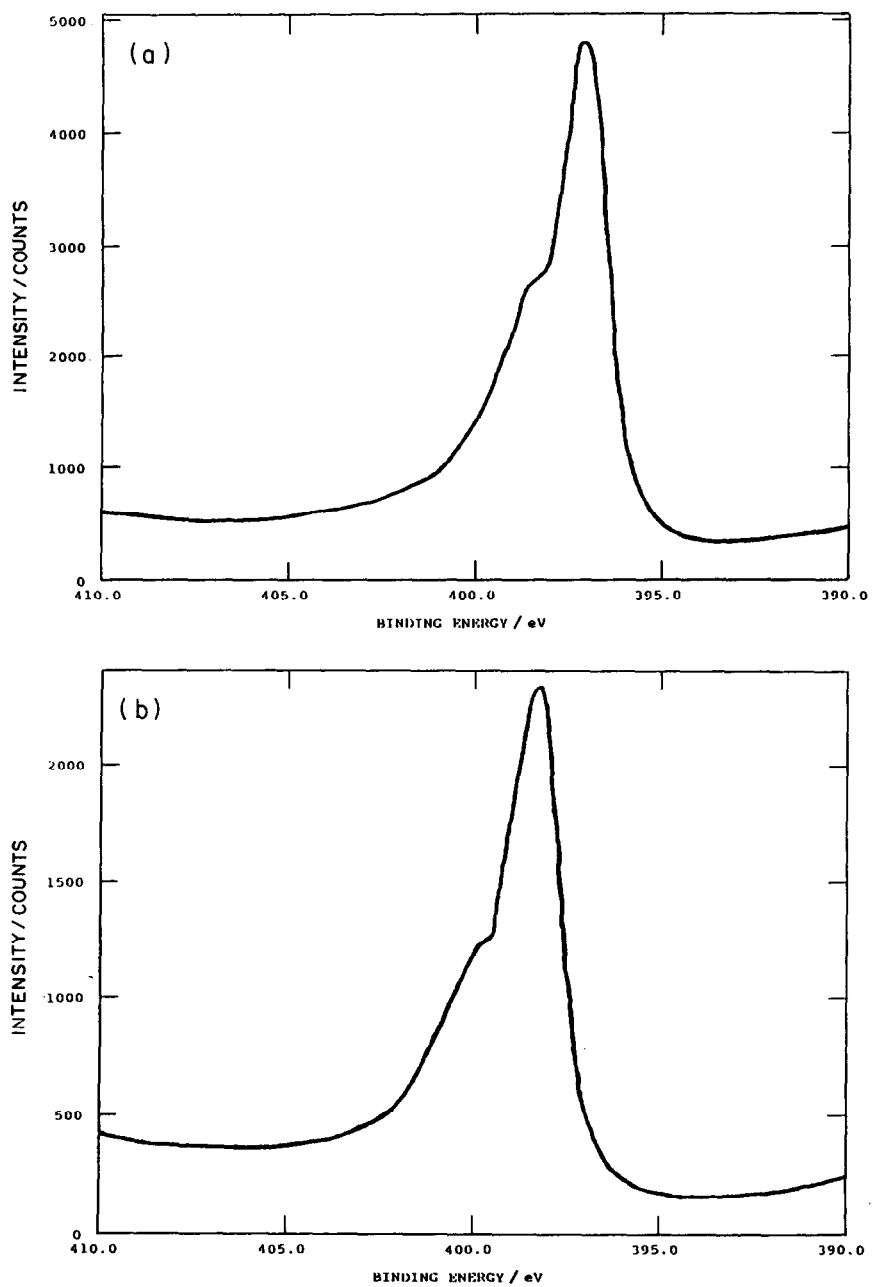


Fig. 13. N 1s spectra of heat-treated FeNPc(1.2) samples loaded at (a) 30% and (b) 40%.

TABLE 3

Atomic ratios for CoNPc(1.2) samples loaded at 27% on Printex XE2

	Non-heat-treated	Heat-treated	Non-heat-treated + H ₂ SO ₄ solution	Heat treated + H ₂ SO ₄ solution
C/N	67	55	40	47
C/O	48	52	20	28
N/Co	18	16	14	18
C/Co	1200	885	552	840
O/Co	25	17	28	30
O/N	1.4	1.1	2	1.7
<i>n</i>	≠ 1.5	2	4	3

the data for iron samples reported in ref. 13 and Table 2 is found in the N/Co ratio which remains constant regardless of heat or solution treatment. In contrast with the iron samples, no demetallation by the acid solution can be detected. An increase in *n* and in oxygen uptake after storage in the acid solution can be seen. According to consideration of eqn. (1), as discussed above, an increase in *n* at constant loading implies a redistribution of catalyst crystallites on the support. At the same loading (27%–30%) the O/N ratio in CoNPc is twice that in FeNPc whereas the *n* values are comparable.

The O 1s spectra of both heat-treated and untreated CoNPc(1.2) samples stored for 10 days in acid solution are similar (Fig. 14). Their shape and position of the maximum are identical with those presented by iron samples and are characteristic of bound oxygen with the maximum at 531.5 eV.

In the case of Co 2p spectra (Fig. 15) the action of the acid solution induces only minor changes for heat-treated samples and no visible modification for untreated samples. Deconvolution of the peak yields about the same amount of Co(II) and Co(III) after storage in acid, and 40% Co(II) and 60% Co(III) for heat-treated samples before exposure to the acid solution.

Figure 16 shows the N 1s spectra for heat-treated and non-heat-treated CoNPc samples before and after storage in acid solution. The most salient feature concerns the effect of the acid solution. On non-heat-treated samples oxidation of the nitrogen atoms is apparent, with the peak maximum shifting from 398.5 to 399.5 eV and the shoulder intensity ratio $I_{400.5}/I_{\max}$ increasing from 0.3 to 0.55. The results presented in Table 3 show that prolonged storage in acid solution results in an increase in the number of catalyst layers and the amount of inserted oxygen. The shift in the position of the N 1s maximum suggests that heat treatment impedes the oxidation of the nitrogen atoms.

It should be noted that the $I_{400.5}/I_{398.5}$ ratio for active CoNPc is much lower than that for both active (10% loading) [13] and less active (30% loading) FeNPc samples, which is characteristic of lower oxidation despite a higher oxygen content. This unusual behavior emphasizes the possible electron-donor rôle of the surface

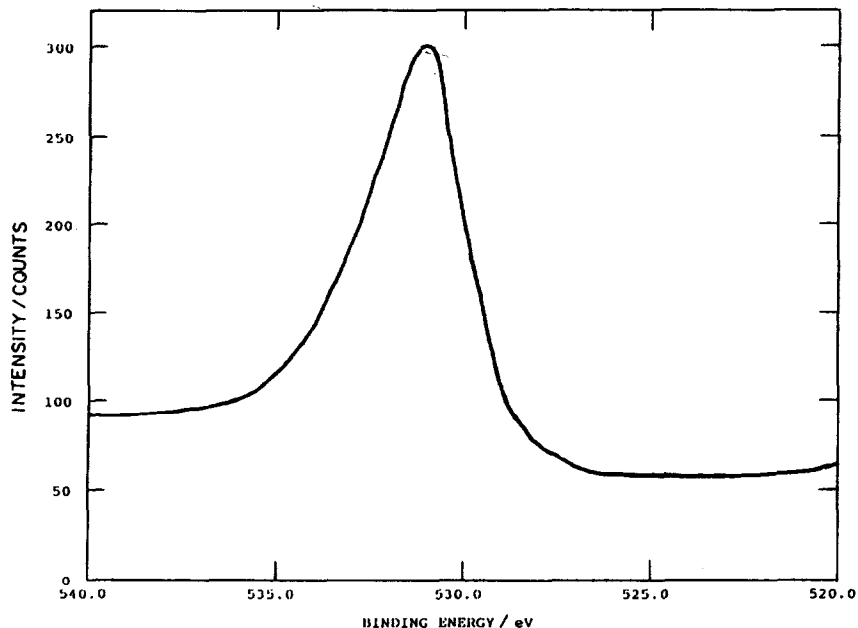


Fig. 14. O 1s spectrum of both FeNpc(1.2) and CoNpc(1.2) after storage for 10 days in acid solutions. No effect of heat treatment was observed.

groups at the catalyst-carbon black interface. Therefore we used the FABS technique to investigate this phenomenon further.

FABS measurements

Depending upon the acceleration voltage applied to the source either negative or positive ions are detected. The positive mode allows the detection of protonation which may take place either in the samples or as a secondary effect in the gas phase during the experiment. In the negative mode no eventual positive protonation is detected, but any negatively charged molecules or radicals will be displayed.

FABS data (intensities versus mass number) obtained in the positive mode for non-heat-treated and heat-treated CoNpc samples after storage for 10 days in acid solution are shown in Figs. 17(a) and 17(b) respectively. Data obtained for these samples in the negative mode are shown in Figs. 17(c) and 17(d) respectively. Figure 17(e) shows negative mode data for the unsupported powder.

The similarity between Figs. 17(a) and 17(b) should be noted. Peaks at mass numbers of 613, 460.1, 443, 307, 289, 153.9, 136.2 and below can be attributed to the NBA matrix, whereas those at 790.1 and 899.2 can be assigned to the samples under investigation. The compound at mass number 790.1 can be identified as a CoNpc molecule protonated and attached to a water molecule. It is not present in the data for the unsupported powder nor in Figs. 17(c) and 17(d). Higher mass

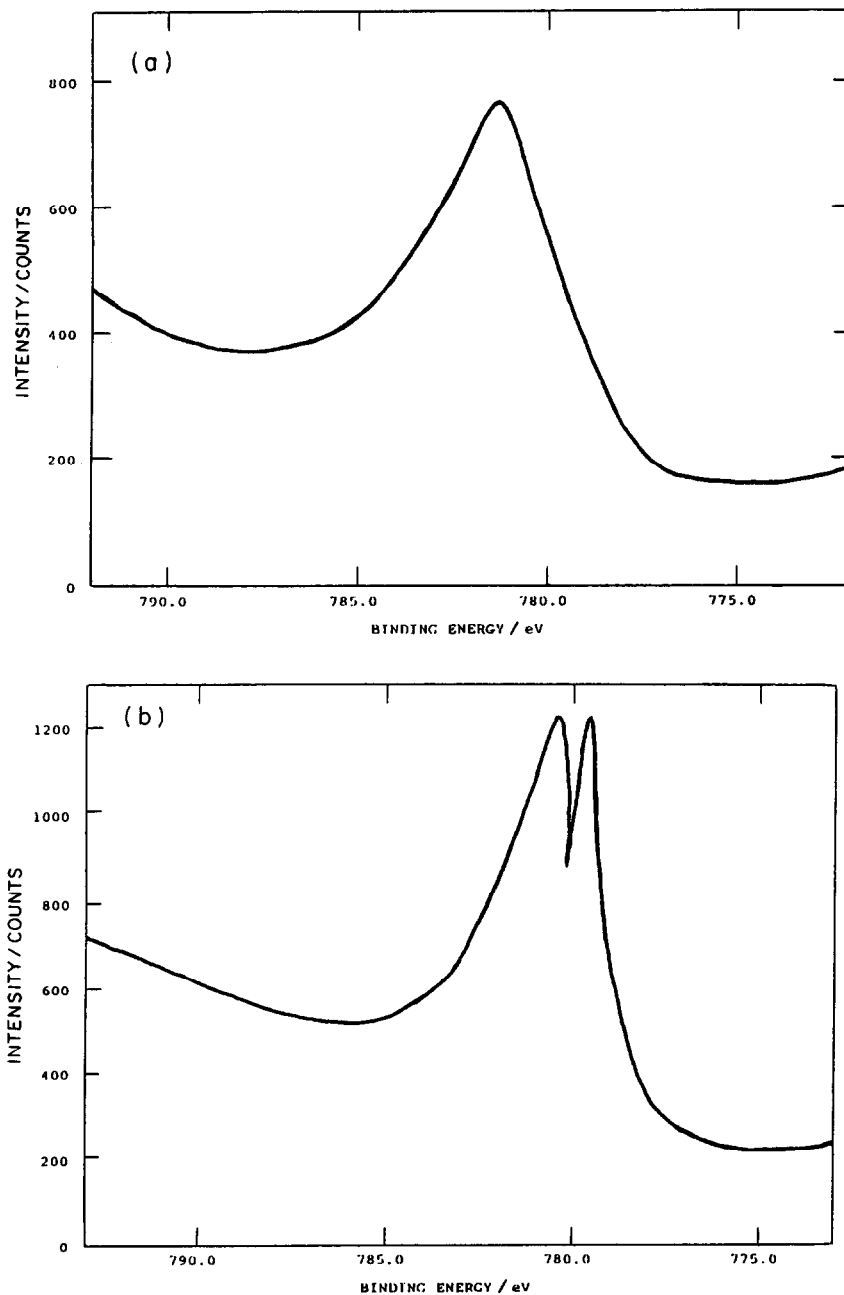


Fig. 15. Co 2p spectra of (a) samples after storage for 10 days in acid solution (heat-treated and non-heat-treated) and (b) heat-treated samples not stored in acid solution.

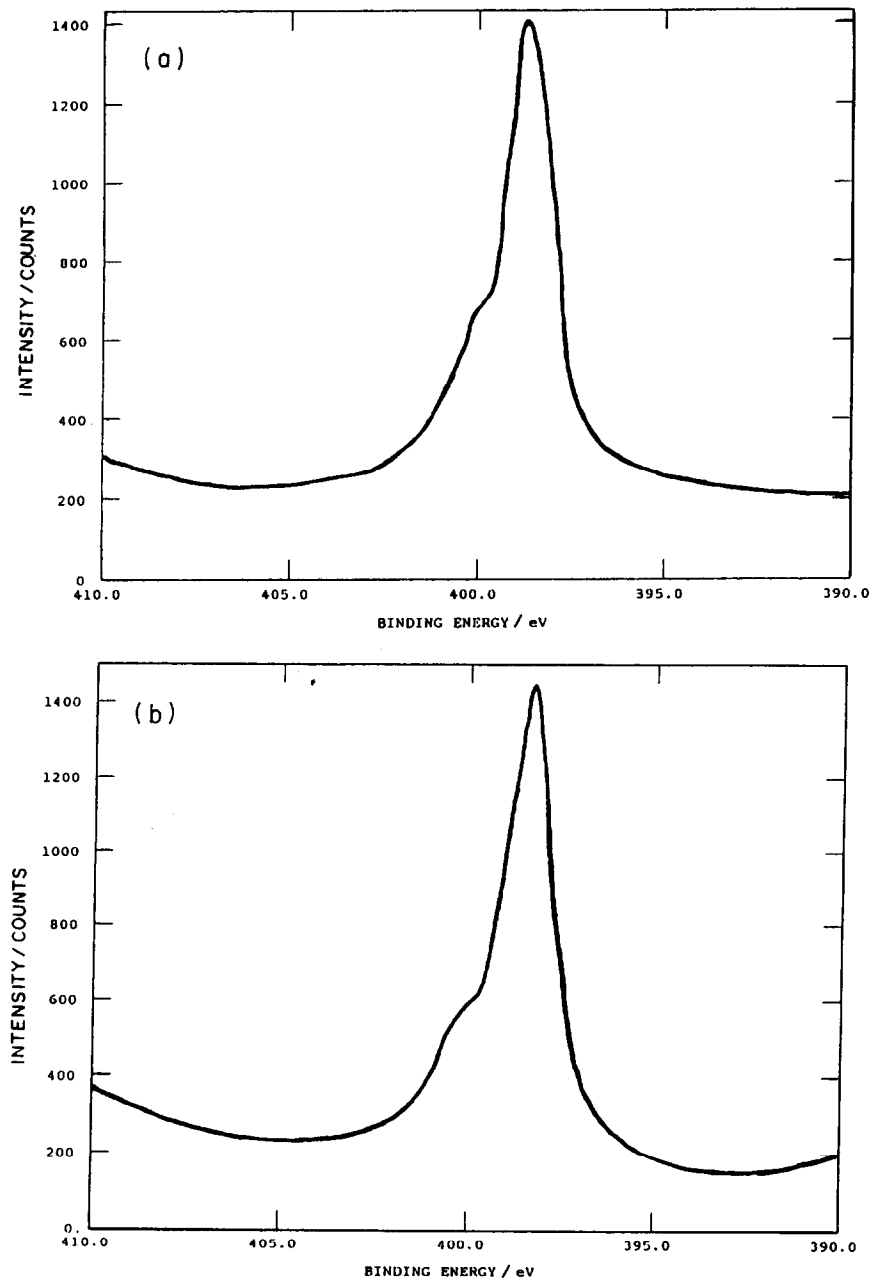


Fig. 16. N 1s spectra of NPcCo(1.2) on Printex XE2: (a) non-heat-treated samples; (b) heat-treated samples; (c) non-heat-treated samples after storage for 10 days in acid solution; (d) heat-treated samples after storage for 10 days in acid solution.

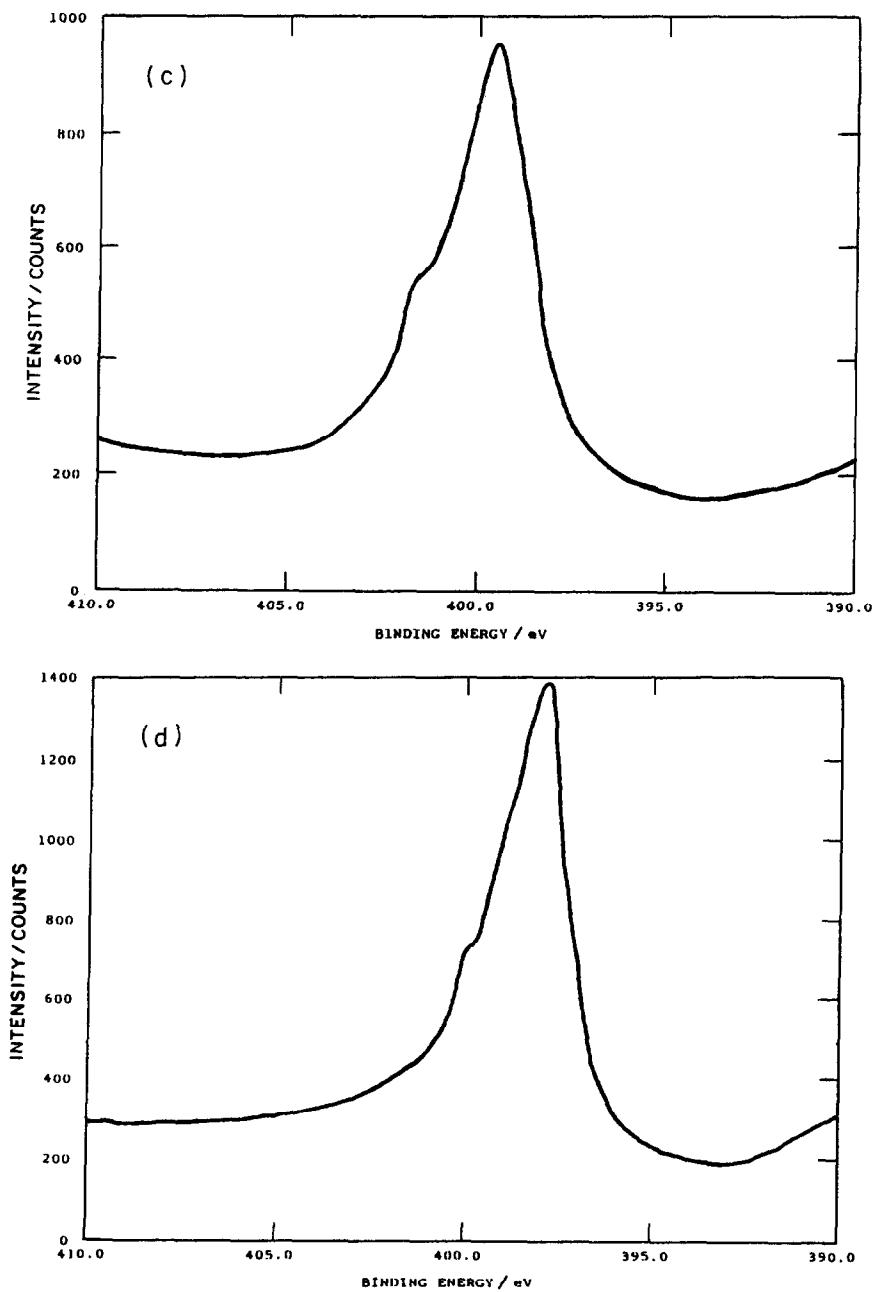


Fig. 16 (continued).

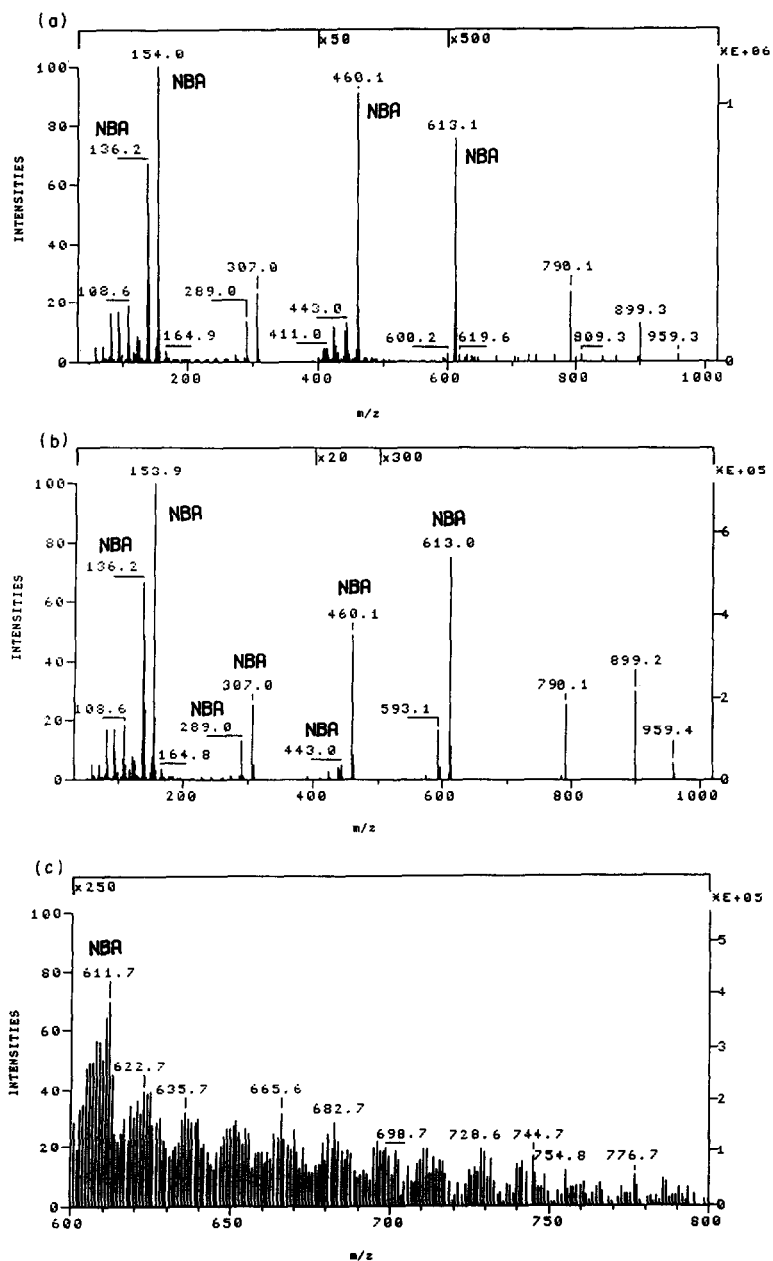


Fig. 17. FAB/MS data (intensities versus mass number) for the CoNPc(1.2) samples loaded at 27% after storage for 10 days in acid solution: (a) non-heat-treated (positive mode); (b) heat-treated (positive mode); (c) non-heat-treated (negative mode); (d) heat-treated (negative mode); (e) unsupported CoNPc(1.2) powder (negative mode).

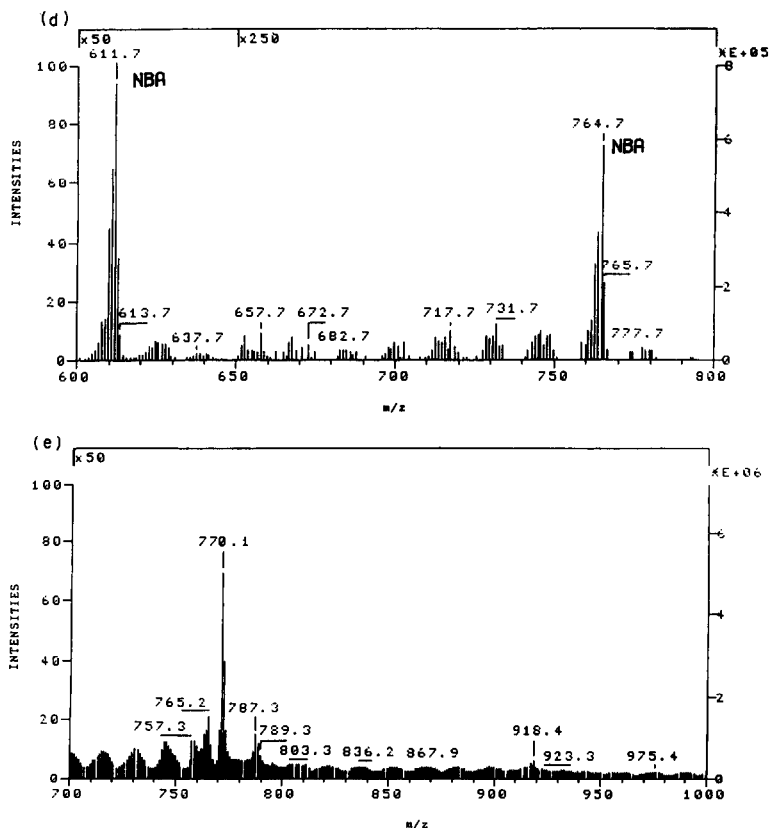


Fig. 17 (continued).

numbers, absent in the unsupported powder, also suggest a chemical bond between CoNpc molecules and the carbon black surface groups.

The major difference between Figs. 17(c) and 17(d) (negative mode data) is the larger number of peaks, forming a quasi-continuum, which are obtained for the non-heat-treated samples. These data emphasize the presence of various possible electron-trapping groups at the carbon black-catalyst interface. During the heat treatment they can act as reservoirs, yielding electrons to the accepting species which, from XPS data, are mainly the O_2 molecules inserted in the catalyst layers. After their elimination, accompanied by oxygen loss, the passage of electrons from the carbon black surface to the oxygen or nitrogen sites may be enhanced. This conclusion is confirmed by the XPS data presented above.

The peak at mass number 764.7 is characteristic of NBA.

CONCLUSION

In this paper the beneficial aspects of substitution of Fe by Co in NPC(1.2) impregnations on an active carbon black support has been shown. Within a useful

range of potentials, electrochemical activities comparable with those of 10% Pt on Vulcan were found.

The application of XPS and FAB/MS techniques has shed some light on the structure of the catalyst layers and on their interactions with the support, yielding some information on the effects of heat treatment. Whereas in the case of FeNPc(1.2) optimal activity is reached for monolayer coverage, improved activities can be obtained using several CoNPc layers. The main difference between CoNPc(1.2) and FeNPc(1.2) catalysts is the absence of demetallation after prolonged exposure to acid solutions for CoNPc.

In the case of FeNPc samples, heat treatment results in an improvement of the dispersion as long as monolayer coverage can take place. This process is accompanied by partial oxidation of the inner nitrogen sites. In the case of CoNPc samples, these sites appear more negatively charged after heat treatment. FAB and XPS data show that this effect can be correlated with the elimination of some electrophilic surface groups at the carbon black-catalyst interface via moderate oxidation by the inserted oxygen molecules. These results emphasize the rôle of the inner nitrogen sites in the electrochemical processes (adsorption and transfer) and stress the electron-donor effect of the carbon black surface groups.

In the case of multilayer catalysts, the substitution of Fe by Co is likely to result in an increase in their conductivity because of the mixture of Co(II) and Co(III).

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